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# Advanced Membranes for Vanadium Redox Flow Batteries (VRFB) Cy Fujimoto

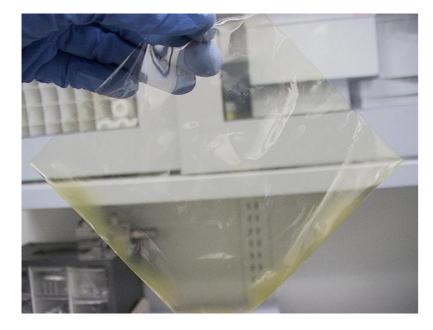
Travis Anderson and Harry Pratt @ SNL; Tom Zawodzinski and Zhijang Tang @ ORNL; Wei Wang and Xiaoling Wei @ PNNL

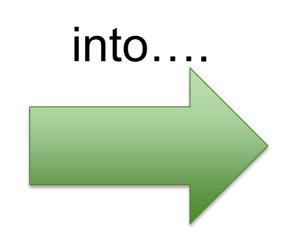






#### DOE has vested interest into turning







#### Customer discovery in vanadium redox flow battery space

- 1. Li ion storage is strongest competitor
- 2. Demonstration VRFB projects are proving to power utilities benefits of flow batteries; timing of commercialization of VRFB 2-4 years
- 3. Market size in US projection relatively small. However, market size increases dramatically by including India and China.
- 4. Cost remains a hurdle, high purity vanadium. However, according to a VRFB CEO, membranes account for a 1/3 of stack cost



Even if SNL develops the perfect membrane, industry will not buy directly from a national lab. Industry wants an industry partner; membranes need to be insured.

License to large

<u>chemical company</u>

+ Instant manufacturing

- Difficult to intro new

product line





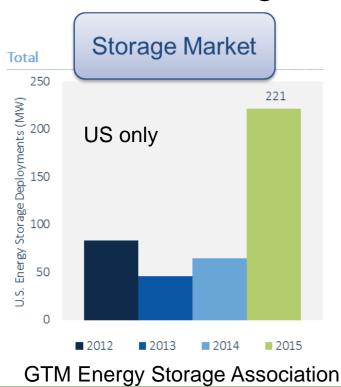


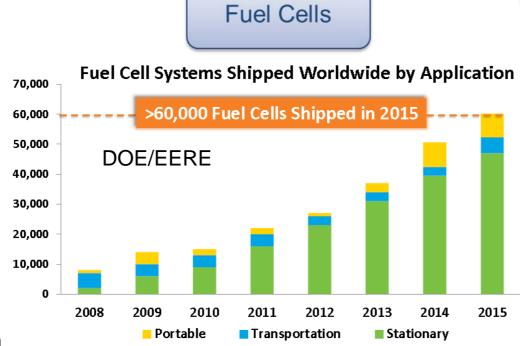
License to small/start up chemical company

- + Nimble, seeking new product as break out
- Manufacturing and insuring product

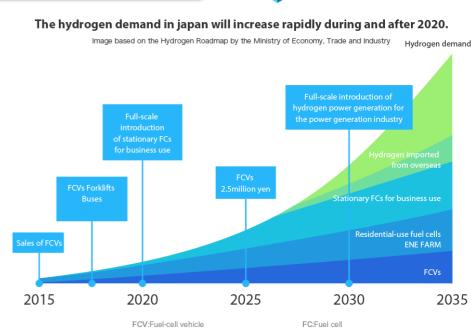
Markets: Instead of focusing on a single market, with the help of

DOE, looking at multiple markets











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Perfluorosulfonic acid membranes (PFSA)s

Company	Product type	Trade name
DuPont now Chemours	Perfluorosulfonic acid membrane	Nafion
Asahi Chemical	Perfluorosulfonic acid membrane	Aciplex
Asahi Glass	Perfluorosulfonic acid membrane	Flemion
3M	Perfluorosulfonic acid membrane	3M MEA
Fumatech	Perfluorosulfonic acid	F-series
Gore	Reinforced perfluorosulfonic acid membrane	GoreSelect
DSM Solutech	Reinforced perfluorosulfonic acid membrane	Solupor

- Various suppliers for perfluorosulfonic acid membranes (PFSA)s
- Primary application chloroalkali industry
- Low production volumes <65 MT/year
- LPV results in high cost \$250-500/m2
- PFSA advocates claim cost of materials "could" reach \$20/m<sup>2</sup> however with no competitor, no real justification to lower costs......



At SNL we are developing and engineering poly(phenylene) membranes to

compete against PFSA.

US Patent 7,301,002

US Patent 7,888,397

US Patent 8,809,483

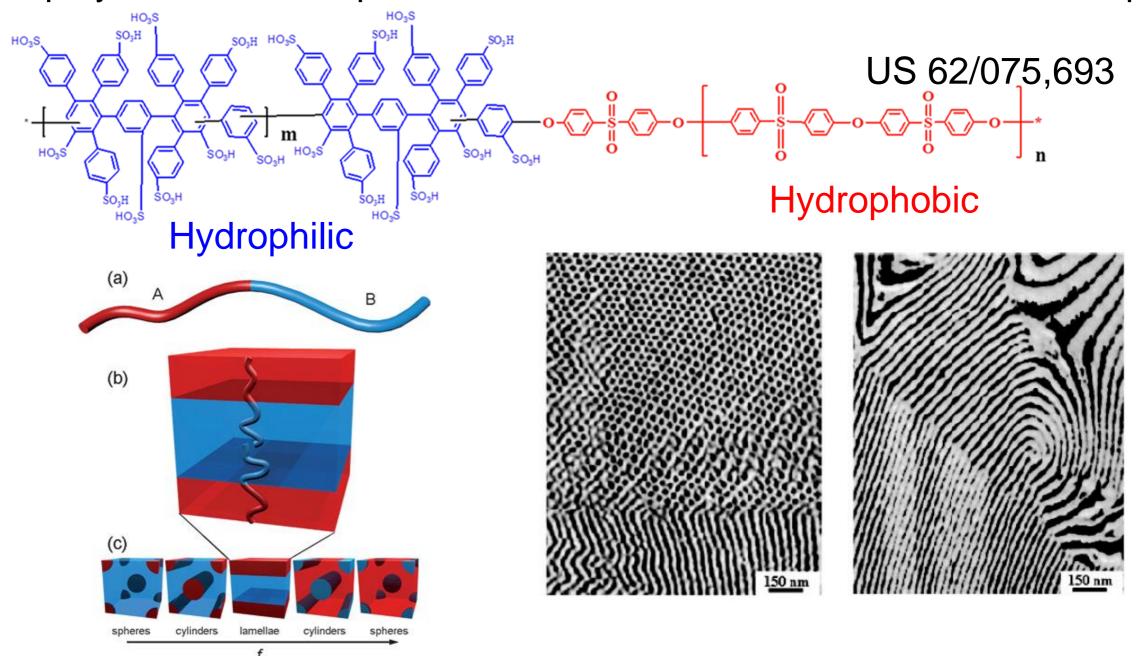
Materials based on chemistry that Dow commercialized as low k dielectric

Low cost at low production volumes

#### **VRFB** membranes



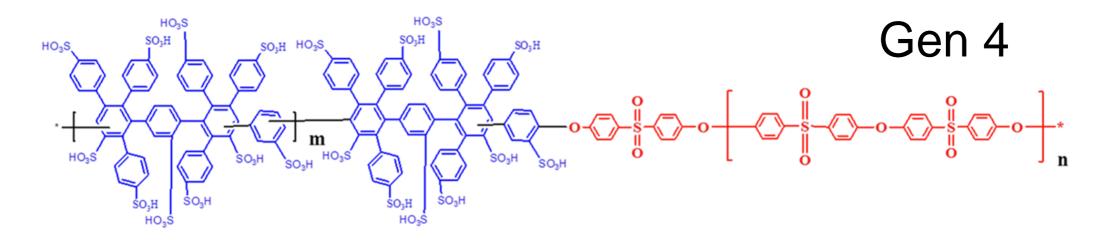
Versatile chemistry allow block co-polymer synthesis Block co-polymers allow for powerful control of water channel size and shape

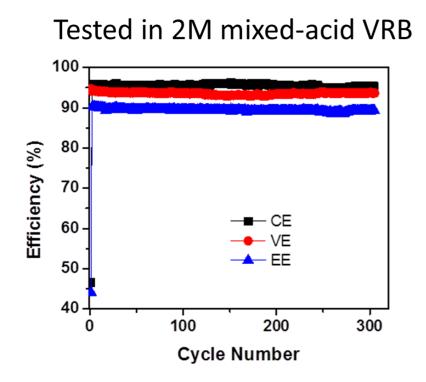


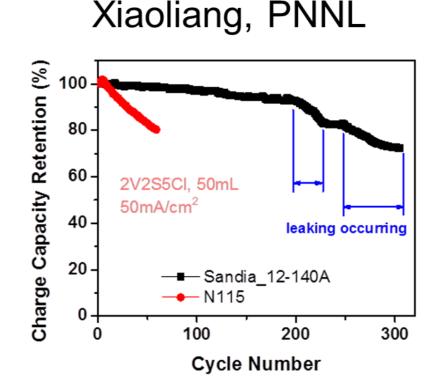
In VRFB, require high transport selective membranes High H+ flux and vanadium barrier

### VRFB Membranes - Durability









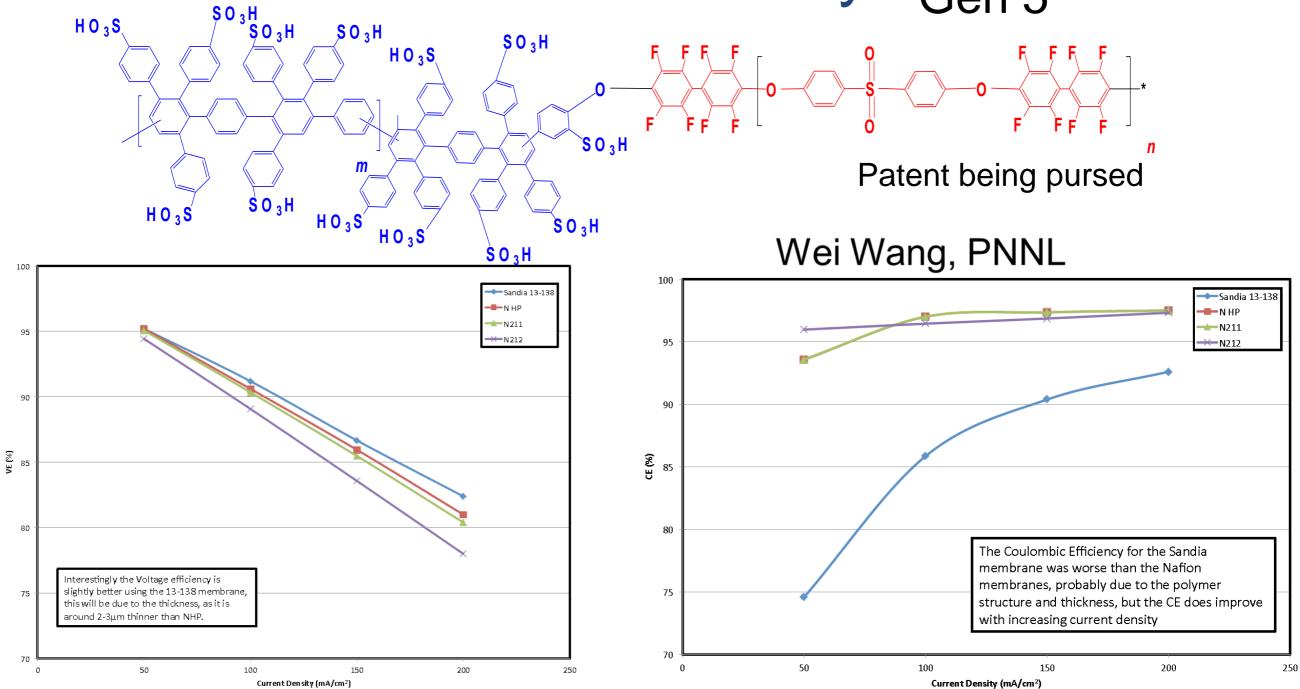


Determined m and n values that resulted in very good selectivity of H+ over vanadium. However, some stability issues.

Due to hydrophobic segment?

# VRFB Membranes - Durability





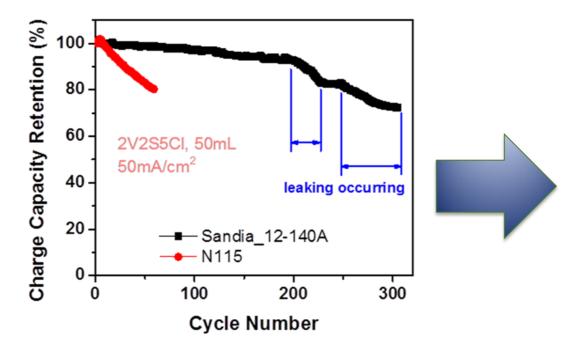
First attempt with new block structure, high conductivity, but selectivity not as high as previous material. Higher capacity loss than Gen4 but wanted to leave sample as long as possible to test durability – **Gen5 much better durability than** 

Gen4! 8

## VRFB Membranes - Durability

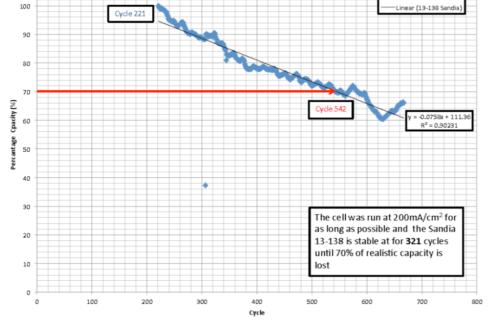














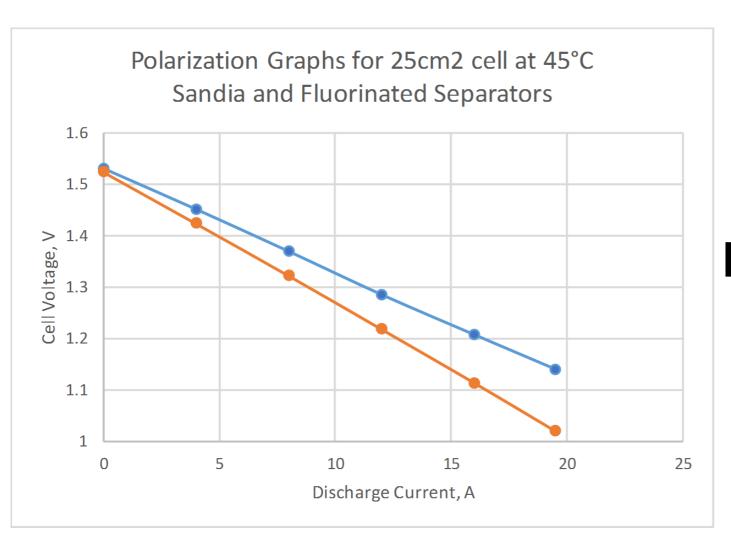
Gen5 has higher chemical stability than Gen4
With PNNL data, improved segment lengths and sent to
VRFB company for testing

#### VRFB Membrane - Performance



Membrane	Efficiency, Round Trip	Efficiency, Coulombic	Efficiency, Voltaic
Sandia	82.2%	96.2%	85.4%
Fluorinated	72.3%	92.5%	78.2%

	Pmax, mW/cm <sup>2</sup>	Specific Resistance, Ωcm <sup>2</sup>
Sandia	1159	0.505
Fluorinated	946	0.610



Cycling Performance Comparison in 25-cm<sup>2</sup> cell at 45°C Sandia and Fluorinated Membranes WattJoule Electrolyte (2M Vanadium)

Data from WattJoule shows Gen5 has higher energy efficiency (+10%). High coulombic efficiency.

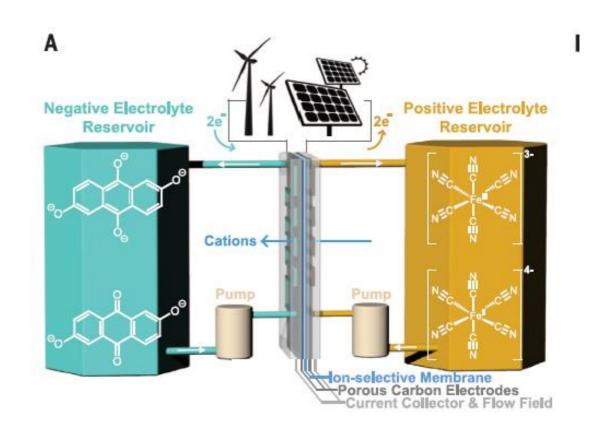


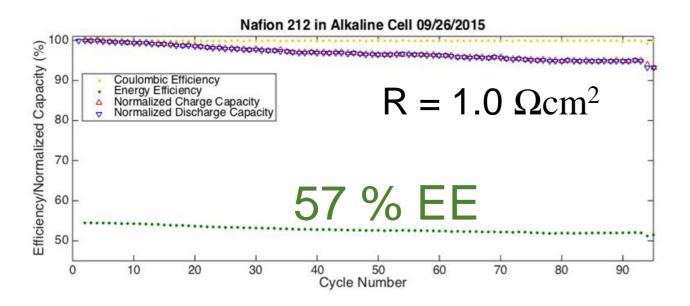
# Beyond Vanadium

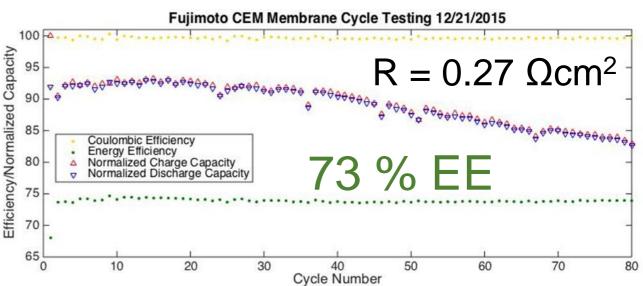


Michael Aziz developing aqueous flow battery with earth abundant materials

Using alkaline enviroment helps improve solubility quinone (increase energy density)







SNL polymer shows ¼ of the resistance of Nafion. Higher energy efficiencies than Nafion (+20%). However, slightly higher capacity loss seen with SNL material.

# Summary/Conclusions



- Growth in energy storage market and clean energy technologies – low cost membranes
- Optimized block co-polymers segments lengths can result in high selectivity and performance
- Gen5 high stability after +600 cycles, best stability in project thus far
- Industry performance testing of Gen5 higher than PFSA

#### **Future Tasks**

- Direction of membrane commercialization
- Long term testing of Gen5 by VRFB industry
- Improve capacity retention of "beyond vanadium" type systems



# Thank You to the DOE OE and especially Dr. Gyuk for his dedication and support to the ES industry and Sandia's ES Program.

Questions?

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